smaller even than in the case of hydrochloric acid, indicating that the unionized H_2SO_4 is formed out of two ions (H^+ and HSO_4^-), in analogy with di-ionic substances, instead of directly out of three ions (H^+, H^+, and $SO_4^=$) in analogy with tri-ionic salts.

Determinations were also made of the transference of sodium, of hydrogen, and of sulphate occurring during the electrolysis of a 0.1 formal solution of sodium hydrogen sulphate at 25°. The results are summarized in Table XIV, on page 1156. Measurements were also made upon the conductance of this salt at various concentrations at 25°. By combining the transference and conductance data the concentrations of the sodium ion and hydrogen ion in the 0.1 formal solution were calculated (in Section 12). The values so obtained are $C_{Na}/C = 0.68$, and $C_H/C = 0.44$.

It has also been shown (in Section 13) that the experiments of Kay on the catalysis of ethyl acetate by 0.1 formal sodium hydrogen sulphate at 35° furnish an independent means of determining the hydrogen-ion concentration, and that the value of C_H/C derived therefrom is 0.416, which agrees well with that (0.44) derived from the transference experiments.

From the values of C_H/C and C_H/C_{Na} derived from the transference and conductance data the concentrations of the other constituents in the 0.1 formal $NaHSO_4$ were computed (in Section 14) with the help of the principle above referred to in regard to the ionization of the first hydrogen of sulphuric acid. In this way C_{HSO_4}/C was found to be 0.44 and C_{SO_4}/C to be 0.34 (see Table XVI).

From these data and also from the corresponding ones for 0.05 formal H_2SO_4 the values of the product $C_HC_{SO_4}/C_{HSO_4}$, the ionization constant of the second hydrogen of sulphuric acid, were calculated to be 0.034 and 0.031, respectively, or in round numbers 3×10^{-2} at concentrations 0.025 to 0.1 formal.

Boston, July, 1910.

ON SURFACE ENERGY AND SURFACE TENSION.

By J. E. Mills and Duncan MacRae.

Received July 25, 1910.

In an article by Whittaker[1] "On the Theory of Capillarity," it was shown that the following empirical relation was apparently true: "*The surface energy of a liquid in contact with its own vapor at any temperature is proportional to the product of the internal latent heat and the (absolute) temperature.*"

The proposed relation and further related applications and inferences have since been discussed by Kleeman in a number of papers.[2]

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[1] *Proc. Roy. Soc.*, 81, 21 (1908).

[2] *Phil. Mag.*, 18, 39, 491, 901 (1909); **19**, 783 (1910)

Some explanation of the relation proposed is perhaps necessary. Particles in the interior of a liquid are attracted by the surrounding molecules equally in every direction; but particles on, or near, the surface are attracted only, or as a resultant, inward, in a direction perpendicular to the surface. When the area of the surface of a liquid is increased, work is therefore done against the molecular forces in bringing additional molecules within the surface layer. If the surface of a liquid is actually increased—as in blowing a soap bubble—it will be found that as the surface increases in size under the action of the externally supplied force (the pressure of the air blown within the bubble), the surface layer of the liquid becomes at the same time colder. Heat is absorbed from the surrounding bodies in order to raise the temperature of the surface film to the initial temperature. Therefore the total energy necessary to increase the surface area is supplied partly as mechanical (external) work and partly as heat energy. If E represents the total energy per square centimeter of surface layer, γ, the necessary mechanical work performed in making this surface, and T the absolute temperature, we have from Helmholtz's free energy equation the relation first stated by Lord Kelvin,

$$1. \qquad E = \gamma - T\frac{d\gamma}{dT},$$

where $-T\,d\gamma/dT$ represents the amount of heat energy absorbed from the surrounding bodies. The mechanically supplied surface energy, γ, in ergs per square centimeter, is numerically equal to the surface tension per linear centimeter in dynes.

The heat of vaporization necessary to change a liquid into a vapor is expended in two ways: *first*, in pushing back the external pressure as the liquid expands, and *second*, in doing certain internal work within the liquid. The first amount of energy is easily calculated and when subtracted from the total leaves the so-called "internal heat of vaporization." This internal heat of vaporization, λ, can be calculated from the thermodynamical relation discovered by Clausius and Clapeyron,

$$2. \qquad \lambda = \left(T\frac{dP}{dT} - P\right)(V - v);$$

here P denotes the vapor pressure, and v and V denote the volume of liquid and its saturated vapor, respectively.

The proposed relation of Whittaker states that

$$3. \qquad \frac{E}{T\lambda} = \text{constant},$$

where E is obtained from equation 1 and λ from equation 2.

Whittaker himself stated that the above empirical relation, being yet without theoretical basis, and being based only on the behavior of five substances over a limited range of temperature, must be received with caution until further comparison with experimental results was possible.

It seemed to the authors desirable, for the reasons mentioned below, to re-examine the experimental basis for the proposed relation.

First.—The values of the internal heat of vaporization used by Whittaker were taken from a paper by one of us[1] and these values have been lately revised. The revision was made necessary by the changes made by Dr. Sydney Young in the original data used for the calculation of these values. These changes were usually small, but extensive, and affected principally the volumes of the saturated vapor at the lower temperatures and the vapor pressure.[2]

Second.—Whittaker, due to the increasing uncertainty in the values for the internal heat of vaporization, and in $d\gamma/dT$ as the critical temperature was approached, did not extend his study of the relation given in equation 3 nearer the critical temperature than 40 or 50°. While it is true that the data become increasingly uncertain, it is also true that λ, E, γ, and $d\gamma/dT$, when plotted against the temperature, give early straight lines over the range of temperature investigated by Whittaker. It becomes of very greatly increased importance therefore to carry the study of equation 3 nearer the critical temperature.

Third.—Whittaker obtained his values of $d\gamma/dT$ from the values for γ as given by Ramsay and Shields.[3] Now they concluded from an apparently sufficient experimental basis that the surface tension, γ, could be expressed for non-associated liquids, as were those investigated by Whittaker, by the equation

$$4. \qquad \gamma(\mathrm{M}v)^{2/3} = k(\tau - d),$$

where τ represents degrees counted from the critical temperature, and k and d are constants, k being approximately 2.12, and d varying with the different substances investigated from 5.9 to 8.5. Mv is the molecular volume of the liquid. Equation 4 is true nearly to the critical temperature, and it is clear that the function $-d\gamma/dT$ must therefore decrease continuously and consistently with increase of temperature; that is, for non-associated liquids $-d\gamma/dT$, when plotted against the temperature, must neither increase nor give a line of double curvature. An examination of the values of $d\gamma/dT$ given by Whittaker for carbon tetrachloride, benzene, and chlorobenzene show that his values do not strictly obey the above statement and seem too greatly influenced by the individual errors of observation. We have changed, therefore, in the tables below, usually only very slightly, some of the values of $d\gamma/dT$ as given by Whittaker for the above-mentioned substances.

Whittaker states on page 23 of the article cited that "A point is at

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[1] Mills, *J. Phys. Chem.*, **8**, 383 (1904); 10, 1 (1906).

[2] Arrhenius number of *Z. physik. Chem.*, **70**, 620 (1910). *Scientific Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

[3] *Phil. Trans. Roy. Soc.*, **184A**, 647 (1893).

length reached, about 180° below the critical point, at which E is stationary, and thenceforward E diminishes as the temperature decreases—a somewhat surprising result. These changes in E are identical with the changes of the function $T\lambda$, which has its stationary point at the same temperature as E." We consider this statement to be in error as regards the behavior of the surface energy so far as non-associated liquids are concerned. The remark seems true for associated liquids. For confirmation of our point of view it is sufficient to cite the form of the surface tension curves as shown in the paper by Ramsay and Shields, and the values of the internal heat of vaporization as given in the papers by Mills already cited.

Fifth.—We found data available for a study also of ethyl acetate, and for the supposedly associated liquids, water, acetic acid, and methyl and ethyl alcohols.

The data and the results obtained are given in the tables below. The surface tension, γ, was obtained from the measurements of Ramsay and Shields.[1] The values of $d\gamma/dT$ were derived from the measurements of γ given, and were smoothed in accordance with the observations above made. The values of $d\gamma/dT$ given by Whittaker were used for ethyl ether and methyl formate at the lower temperatures, and his values were not greatly changed for carbon tetrachloride and benzene. The values for E were obtained from the data given by the use of equation 1. The

TABLE I.—ETHYL OXIDE.

t° C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	16.49	....	....	80.04	....
40	14.05	0.112	49.1	75.02	20.9
50	12.94	0.1115	48.9	72.66	20.8
60	11.80	0.110	48.4	70.40	20.6
70	10.72	0.108	47.8	67.81	20.6
80	9.67	0.106	47.1	65.40	20.4
90	8.63	0.1035	46.1	62.89	20.2
100	7.63	0.1015	45.5	60.40	20.2
110	6.63	0.0995	44.7	57.53	20.3
120	5.65	0.097	43.8	54.53	20.4
130	4.69	0.094	42.6	51.43	20.6
140	3.77	0.0905	41.1	48.13	20.7
150	2.88	0.086	39.3	44.30	21.0
160	2.08	0.080	36.7	39.81	21.3*
170	1.33	0.071	32.8	34.31	21.6*
180	0.64	0.058	26.9	27.36	21.7*
185	0.38	0.0495	23.0	22.99	21.8*
190	0.16	0.040	18.7	16.59	24.3*
193	0.04	....	....	9.71	....
193.8	0	....	....	0	....
190	Mills	....	....	17.68	22.8*
190	Dieterici	....	....	17.44	23.2*

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[1] *Phil. Trans.*, **184**A, 647 (1893); *Z. physik. Chem.*, **12**, 433 (1893).

values given for λ were calculated by Mills and have been partially published.[1] Details and references will be found in that paper. The complete data will be published later.

We have, except for the alcohols, averaged the values of the constant $10^4E/T\lambda$ for each substance down to the values marked with an asterisk, and have marked with an asterisk all values differing from the mean values so obtained by more than 3 per cent. The mean values are given in Table XI.

Considering first the non-associated substances, it will be seen that the "constant" decreases to the extent of 3 per cent. or more from its value at the lowest temperature to a minimum value, and then rises in value until the critical temperature is reached. This consistent behavior of the constant tends strongly to show that it is not a true constant. A closer examination of the data tends to confirm this belief.

For the divergence of the "constant" from constancy cannot be due to the values used for the internal heats of vaporization. One of us has made an extended and close study[2] of the internal heat of vaporization both of the substances at present under investigation and of other substances. From the discussion and data given in the papers cited we feel certain

TABLE II.—CARBON TETRACHLORIDE.

$t°$ C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	25.68	....	....	....	....
80	18.71	....	....	41.64	....
90	17.60	0.1115	58.1	40.72	39.3*
100	16.48	0.110	57.5	39.64	38.9
110	15.41	0.1085	57.0	38.53	38.6
120	14.32	0.107	56.4	37.48	38.3
130	13.27	0.105	55.6	36.35	38.0
140	12.22	0.103	54.8	35.27	37.6
150	11.21	0.1015	54.1	34.19	37.4
160	10.22	0.100	53.5	33.28	37.2
170	9.24	0.098	52.6	32.21	36.9
180	8.26	0.0965	52.0	30.83	37.2
190	7.28	0.095	51.3	29.52	37.5
200	6.34	0.093	50.3	28.22	37.7
210	5.40	0.0915	49.6	26.83	38.3
220	4.47	0.090	48.8	25.35	39.0
230	3.56	0.0870	47.3	23.73	39.6*
240	2.74	0.0825	45.1	21.91	40.1*
250	1.93	0.076	41.7	19.85	40.2*
260	1.20	0.067	36.9	17.15	40.4*
270	0.59	....	....	13.62	....
283.15	0	....	....	0	....
260	Mills	....	....	16.78	41.2*
260	Dieterici	....	....	16.97	40.8*

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[1] THIS JOURNAL, 31, 1099 (1909).

[2] Mills, *Ibid.*, 31, 1099 (1909). *J. Phys. Chem.*, 13, 512 (1909).

TABLE III.—BENZENE.

t° C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
80	20.28	0.116	61.2	86.70	20.0
90	19.16	0.116	61.3	84.69	19.9
100	18.02	0.116	61.3	82.37	20.0
110	16.86	0.115	60.9	79.98	19.9
120	15.71	0.1145	60.7	77.39	20.0
130	14.57	0.1125	59.9	75.45	19.7
140	13.45	0.1105	59.1	73.45	19.5
150	12.36	0.108	58.0	71.34	19.2
160	11.29	0.106	57.2	69.48	19.0
170	10.20	0.104	56.3	67.25	18.9
180	9.15	0.102	55.4	65.21	18.8
190	8.16	0.100	54.5	62.51	18.8
200	7.17	0.098	53.5	59.75	18.9
210	6.20	0.096	52.6	57.04	19.1
220	5.25	0.094	51.5	53.76	19.4
230	4.32	0.091	49.9	50.30	19.7
240	3.41	0.087	48.1	46.53	20.1*
250	2.56	0.083	46.0	42.46	20.7*
260	1.75	0.0785	43.6	37.55	21.8*
270	0.99	0.073	40.6	31.49	23.7*
275	0.66	....	....	...	....
280	0.29	....	....	23.45	....
288.5	0	....	....	0	....
270	Mills	....	....	31.47	23.7*

Dieterici not calculated at 270°, but at 260° = 37.52 and at 280° = 23.79.

TABLE IV.—CHLOROBENZENE.

t° C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
150	17.67	0.100	60.0	65.45	21.7
160	16.62	0.0995	59.7	64.14	21.5
170	15.67	0.0995	59.8	62.87	21.5
180	14.66	0.099	59.5	61.67	21.3
190	13.69	0.0985	59.3	60.06	21.3
200	12.72	0.0970	58.6	58.50	21.2
210	11.75	0.0960	58.1	56.87	21.1
220	10.81	0.0945	57.4	55.55	21.0
230	9.88	0.093	56.7	53.90	20.9
240	8.94	0.0915	55.9	52.25	20.9
250	8.04	0.090	55.1	50.37	20.9
260	7.14	0.0875	53.8	48.17	21.0
270	6.27	0.0855	52.7	45.80	21.2
280	5.40	0.0825	....	...	....
290	4.54	0.080	....	...	....
300	3.79	0.0765	....	...	....
310	3.05	0.073	....	...	....
320	2.35	0.069	....	...	....
333	1.47	....	....	...	....
359.1	0	....	....	....	....

TABLE V.—METHYL FORMATE.

t° C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	24.62	....	....	....	....
30	23.09	0.153	69.4	104.38	21.9
40	21.56	0.151	68.8	101.16	21.7
50	20.05	0.149	68.2	98.18	21.5
60	18.58	0.147	67.5	94.74	21.4
70	17.15[1]	0.145	66.9	91.43	21.3
80	15.70	0.143	66.2	88.31	21.2
90	14.29	0.141	65.5	85.25	21.2
100	12.90	0.139	64.6	81.83	21.2
110	11.52	0.1365	63.8	78.96	21.1
120	10.18	0.134	62.9	75.87	21.1
130	8.86	0.1315	61.8	71.95	21.3
140	7.54	0.128	60.4	68.10	21.5
150	6.30	0.124	58.8	64.03	21.7
160	5.06	0.119	56.6	59.28	22.0
170	3.90	0.1125	53.7	54.41	22.3*
180	2.81	0.105	50.4	48.64	22.9*
190	1.78	0.096	46.2	41.93	23.8*
200	0.87	0.086	41.5	33.18	26.5*
210	0.06	...	....	19.58	....
214.0	0	..	....	0	....
200	Mills	...	....	35.10	25.0*
200	Dieterici	...	....	35.04	25.0*

TABLE VI.—ETHYL ACETATE.

t° C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	23.60	....	....	...	....
80	16.32	0.1185	58.1	78.25	21.1
90	15.14	0.117	57.6	76.40	20.8
100	13.98	0.115	56.9	74.36	20.5
110	12.84	0.113	56.1	72.13	20.3
120	11.75	0.111	55.4	69.64	20.2
130	10.66	0.109	54.6	66.84	20.3
140	9.57	0.107	53.8	64.42	20.2
150	8.52	0.1045	52.7	61.38	20.3
160	7.48	0.1025	51.9	58.36	20.5
170	6.47	0.100	50.8	55.71	20.6
180	5.51	0.097	49.4	52.68	20.7
190	4.54	0.093	47.6	49.48	20.8
200	3.64	0.089	45.7	46.11	21.0
210	2.80	0.0835	43.1	42.08	21.2
220	1.96	0.077	39.9	37.11	21.8*
230	1.18	0.069	35.9	31.32	22.8*
240	0.49	0.060	31.3	23.55	25.9*
245	0.21	....	....	18.00	....
250.1	0	....	....	0	....
240	Mills	....	....	24.78	24.6*
240	Dieterici	....	....	24.32	25.1*

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[1] Misprinted in the original paper by Ramsay and Shields.

that the heats of vaporization given are correct to within 2 per cent. except as the critical temperature is approached. Nearly always they are correct to within 1 per cent. Now as the critical temperature is approached, it is true, as shown in the papers cited, that the internal heat of vaporization as usually calculated by the use of equation 2, and as given in this paper, is too small. But the error thus caused is not nearly great enough to account for the great increase in the value of the constant.

TABLE VII.—WATER.

$t°$ C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
0	73.21	0.122	106.5	565.0	6.90
10	71.94	0.131	109.0	559.3	6.89
20	70.60	0.1385	111.2	552.5	6.87
30	69.10	0.1475	113.8	545.8	6.88
40	67.50	0.155	116.0	539.2	6.88
50	65.98	0.162	118.3	532.4	6.88
60	64.27	0.168	120.2	525.4	6.87
70	62.55	0.174	122.2	518.4	6.87
80	60.84	0.179	124.0	511.4	6.87
90	58.92	0.1835	125.5	504.5	6.85
100	57.15	0.188	127.3	497.1	6.87
110	55.25	0.192	128.8	489.2	6.87
120	53.30	0.196	130.3	481.0	6.89
130	51.44	0.200	132.0	472.9	6.92
140	49.42	0.204	133.7	465.0	6.96

TABLE VIII.—ACETIC ACID.

$t°$ C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	23.46	....	....	79.17	....
130	16.18	0.083	49.6	85.09	14.5
140	15.32	0.085	50.4	83.62	14.6
150	14.46	0.0865	51.0	82.37	14.6
160	13.58	0.088	51.7	81.14	14.7
170	12.71	0.089	52.1	81.85	14.4
180	11.77	0.090	52.5	79.01	14.7
190	10.93	0.091	53.1	77.97	14.7
200	10.05	0.092	53.6	76.72	14.8
210	9.11	0.0923	53.7	75.32	14.8
220	8.22	0.0927	53.9	73.25	14.9
230	7.28	0.0930	54.1	71.44	15.0
240	6.36	0.0930	54.1	69.54	15.1
250	5.40	0.0930	54.0	67.05	15.4*
260	4.48	0.0915	53.2	64.00	15.6*
270	3.59	0.0885	51.6	60.37	15.8*
280	2.71	0.084	49.2	55.97	15.9*
290	1.92	0.0785	46.1	50.32	16.3*
300	1.16	0.0710	41.8	42.97	17.0*
310	0.49	....	....	33.06	....
320	0.32	....	....	18.27	....
321.65	0	....	....	0	....

TABLE IX.—METHYL ALCOHOL.

t° C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	23.02	....	....	266.5	....
70	17.64	....	....	244.4	....
80	16.70	0.0905	48.6	238.5	5.77
90	15.72	0.093	49.5	232.1	5.87
100	14.80	0.0955	50.4	225.2	6.00
110	13.85	0.098	51.4	218.3	6.14
120	12.88	0.1005	52.4	211.0	6.32
130	11.84	0.103	53.3	203.2	6.51
140	10.79	0.1055	54.4	195.4	6.74
150	9.77	0.108	55.4	185.6	7.06
160	8.65	0.1105	56.5	178.2	7.32
170	7.53	0.113	57.6	168.5	7.71
180	6.41	0.1155	58.7	158.1	8.19
190	5.23	0.117	59.4	147.5	8.70
200	4.05	0.117	59.4	134.9	9.31
210	2.93	0.114	58.0	119.5	10.05
220	1.80	0.108	55.0	99.6	11.21
230	0.77	0.093	47.5	74.6	12.67
234	0.42	...	....	61.9	...
236	0.27	...	....	54.4	...
240.0	0	...	....	0	...

TABLE X.—ETHYL ALCOHOL.

t° C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	22.03	....	....	208.0	....
40	20.20	0.0873	47.5	205.3	7.39
60	18.43	0.091	48.7	199.2	7.35
80	16.61	0.0943	49.9	191.6	7.38
90	15.63	0.096	50.5	186.6	7.45
100	14.67	0.098	51.2	181.8	7.55
110	13.69	0.0995	51.8	174.9	7.73
120	12.68	0.1015	52.6	168.8	7.92
130	11.63	0.103	53.1	162.1	8.14
140	10.59	0.105	53.9	155.7	8.39
150	9.52	0.107	54.8	149.3	8.67
160	8.45	0.1085	55.4	141.7	9.03
170	7.34	0.1105	56.3	133.6	9.51
180	6.23	0.112	57.0	124.9	10.1
190	5.13	0.112	57.0	114.8	10.7
200	3.99	0.1105	50.7	104.0	11.5
210	2.91	0.1065	54.3	91.8	12.3
220	1.87	0.100	51.2	78.3	13.3
230	0.91	0.089	45.7	62.5	14.5
234	0.59	0.082	....	....	....
236	0.43	0.077	....	....	....
240	0.15	...	....	35.6	....
243.1	0	...	....	0	...

For it was further shown that the true heat of vaporization, even in the immediate neighborhood of the critical temperature, can be very closely obtained by means of two equations, one proposed by Mills and the other by Dieterici. Values thus obtained, designated Mills and Dieterici, respectively, are given in the tables for comparison, and the constant shown as calculated from them. But one conclusion is possible when the papers cited and the results shown have been studied: *The increase in the value of the constant near the critical temperature is not largely due to errors in the values of the heats of vaporization used.*

Are then the surface tension measurements in error? The surface tensions used were calculated by Ramsay and Shields from the rise of the liquid in a capillary tube by means of the formula

5. $$\gamma = \tfrac{1}{2}\, r.\, h.\, g.\, (d - D),$$

where r is the radius of the tube, h is the height to which the liquid is raised, g is the gravitation constant, and d and D are the densities of the liquid and its saturated vapor at the temperature of the experiment. Since errors in r and g could not thus affect the result, we have only to consider the probable size of the errors in h and in $d - D$. There seems no good reason to suppose that large and regular errors were made in the determinations of the height of the rise of the liquid in the capillary tube. Regarding the possibility of errors in $d - D$, it is clear that, since d approaches D in value as the critical temperature is approached, errors of measurement of the densities will be greatly multiplied near the critical temperature in their effect upon γ. But the well-known form of the density curves and the law of "rectilinear diameters" aids greatly in smoothing out individual errors of observation. The papers of Ramsay and Shields do not state from what source the densities were obtained, but comparison makes it fairly certain that the measurements for ethyl oxide and water (except the densities for these two substances of the liquid to 100°), methyl and ethyl alcohols, and acetic acid were by Ramsay and Young; for methyl formate and ethyl acetate by Young and Thomas; for benzene, chlorobenzene, and carbon tetrachloride by Young. The measurements of these investigators, as is well known, are exceedingly accurate and would introduce only comparatively small errors in γ. (We would note a misprint in the density of methyl formate, liquid at 140°, 0.7368 for 0.7638; also in accordance with Young's data, carbon tetrachloride vapor at 230° should be 0.1232; benzene at 280° should be 0.1660; and ethyl alcohol at 200° should be 0.5568 for the liquid. The values for acetic acid have been revised by Young, the only changes of significance for our purpose being at 280° where the density of the liquid should be 0.6629 and of the vapor 0.0883; and at 320° for the vapor, which should be 0.2421. These changes will not affect the character of the results shown in the tables.) We conclude therefore *that the sur-*

face tension measurements are fairly accurate and cannot directly cause the variation shown in the constant.

A relatively very large error is introduced in the determination of $d\gamma/dT$. For near the critical temperature $-T\, d\gamma/dT$ becomes very large compared to γ and errors in $d\gamma/dT$ affect the constant almost proportionately. In determining $d\gamma/dT$ we deal with the difference of measurements of γ in themselves nearly equal and subject to some individual error. We would be inclined to think that with any one substance the error introduced into the constant through the uncertainty of the factor $d\gamma/dT$ might be quite sufficient to explain the rise in the value of the constant at the critical temperature. But there seems no reason to suppose that the error thus introduced would always be large and in the same direction, unless there is some undiscovered defect in the determination of the surface tension. Nor is it reasonable to suppose that the consistently recurring decrease, even though it be small, in the value of the constant at low temperatures, is to be attributed to chance errors in the measurements.

The authors therefore conclude *that the variation of the constant in the relation, $E/T\lambda$ = constant, proposed by Whittaker, is not due to the measurements used in testing the relation, but to the fact that the relation is only approximately true.*

With regard to the associated liquids, as was to be expected, the constant makes no pretense of constancy for the alcohols. But contrary to expectation, the constant remains as near a constant for water and acetic acid as it does for the non-associated liquids. We have no idea of the reason for this behavior.

It is seldom that any physical relation holds exactly true throughout a wide range of temperature. It is therefore quite reasonable to study further the relation stated by Whittaker and to seek a possible cause for the same. One of the authors in a paper already cited has discussed theoretically, and carefully tested by means of the extensive series of exact measurements available, the three following equations for the internal heat of vaporization:

$$2.\quad \lambda = \left(T\frac{dP}{dT} - P\right)(V - v) = 0.0_43183\left(T\frac{dP}{dT} - P\right)(V - v) \text{ calories.}$$

$$6.\quad \lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) \text{ calories.}$$

$$7.\quad \lambda = CRT\, ln\, \frac{d}{D} = 4.77\, C\, \frac{T}{m} \log \frac{d}{D} \text{ calories.}$$

Equation 2 is the thermodynamical equation already mentioned. In obtaining the constant the pressure is expressed in millimeters of mercury, and v and V are the volumes occupied by a gram of the liquid and of its saturated vapor.

In equation 6 μ' is a constant for any particular non-associated liquid,

d is the density of the liquid, and D is the density of the saturated vapor. The values of μ' for the substances studied in this paper are given in Table XI. The equation was deduced theoretically by Mills from assumptions regarding the molecular attraction and has been extensively studied[1] and would seem to be exactly true for normal non-associated liquids.

In equation 7 C is a constant for any particular substance, having approximately the same value, 1.755, for all normal non-associated liquids, R is the usual gas constant, and d and D represent densities as before. The values for C are given in Table XI. The equation was first proposed as an empirical equation by Dieterici[2] and has been further studied by Richter[3] and by Mills.[4]

Inserting the values of E and λ from equations 1 and 2 in equation 3, we get,

$$8. \qquad \frac{\gamma - T\dfrac{d\gamma}{dT}}{T\left(T\dfrac{dP}{dT} - P\right)(V - v)} = \text{constant},$$

as the form of the relation already studied. Now if it were possible to get the limit of this equation at the critical temperature a further test of its truth could be applied. This does not seem possible with our present knowledge. γ probably falls out and T cancels, leaving

$$\frac{d\gamma}{dT}\Big/\left(T\frac{dP}{dT} - P\right)(V - v)$$

as the indigestible form of the equation. The combination of the equations 1, 2 and 3 under approximate conditions has been studied by Kleeman in the papers cited.

Next combining the relation given in equation 6 with that of Whittaker we obtain, calling the constant of Whittaker's relation k,

$$9. \qquad E = k\mu' T(\sqrt[3]{d} - \sqrt[3]{D}).$$

The values of $k\mu'$ are given in Table XI, though we have as yet been able to draw no conclusion from their product. That the surface energy of a liquid should be proportional to the product of the absolute temperature and the difference of the cube roots of the densities of the liquid and vapor is very suggestive. For it has been shown in the papers by Mills already cited that equation 6 expresses a relation between the molecular attractive forces, and that this relation leads to the conclusion that $\mu' \sqrt[3]{d}$ is the energy necessary to overcome the molecular attraction in pulling

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[1] *J. Phys. Chem.*, **6**, 209 (1902); 8, 383 (1904); **8**, 593 (1904); **9**, 402 (1905); **10**, 1 (1906); **11**, 132 (1907); **11**, 594 (1907); **13**, 512 (1909). THIS JOURNAL, **31**, 1099 (1909).

[2] *Ann. Physik*, **12**, 144 (1903).

[3] "Ueber die innerer Verdampfungswärme," Rostock, 1908.

[4] THIS JOURNAL, **31**, 1099 (1909).

the molecules of a liquid apart to an infinite distance. Similarly $\mu' \sqrt[3]{D}$ would represent the energy necessary to pull apart the molecules of a vapor to an infinite distance, the temperature of the vapor remaining constant. Now the so-called liquid surface is really the resultant of two surface layers, the one of the liquid and the other of its vapor, in contact, with oppositely directed forces. Hence it would seem that the total surface energy of a liquid, as usually so-called, can be divided into two parts, one part due to the liquid E_L and the other part due to the vapor over the liquid E_V, the resultant forces being oppositely directed and the surface energy of opposite sign from the standpoint of a surface molecule. We can then write the equations:

10. $$E_L = K'T\sqrt[3]{d}.$$

11. $$E_V = K'T\sqrt[3]{D}.$$

12. $$E_L - E_V = E = K'T(\sqrt[3]{d} - \sqrt[3]{D}).$$

Perhaps equations 10, 11, and 12 do not express a point of view entirely new so much as they serve merely to add emphasis and give a quantitative expression to a fact already well known,[1] namely, that the nature of the surrounding gas influences the surface tension. It would seem from the suggested equations that perhaps the amount of such influence has been greatly underestimated.

It would seem probable that if equations 10, 11 and 12 are true, the surface tension as usually measured should similarly be capable of division into two parts, one part due to the liquid surface, the other part due to the gaseous surface over the liquid. Such a process of division might result in finding simpler and more accurate relations between the surface tension and other quantities. Search by one of us for the proper modification to be applied to the liquid surface tension as usually measured in order to eliminate the effect of the vapor has apparently met with success, and if a full investigation confirms the results already derived the investigation will shortly be published.

TABLE XI.

	Molecular weight.			$10^4E/Tl.$		
	$m.$	$\mu'.$	$C.$	$10^4k.$	$10^4\mu'k.$	$10^4Ck.$
Ethyl oxide..........	74.08	103.76	1.724	20.56	2132	3544
Carbon tetrachloride...	153.8	44.01	1.667	38.00	1672	6335
Benzene.............	78.05	109.26	1.690	19.42	2122	3282
Chlorobenzene........	112.49	81.66	1.714	21.19	1730	3631
Methyl formate.......	60.032	119.86	1.706	21.44	2570	3657
Ethyl acetate.........	88.064	98.88	1.812	20.61	2038	3735
Water...............	18.016	555.1*	...	6.85	3802	....
Acetic acid...........	60.032	....	...	14.74	....	....
Methyl alcohol........	32.032	305.0*	...	5.88*	1794	....
Ethyl alcohol.........	46.048	240.9*	...	7.42*	1787	....

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[1] See paper by Ramsay and Shields already cited, page 666, and similar determinations by others.

* Not constant.

If the value of λ from equation 7 be used in the equation 3 proposed by Whittaker we have

$$13. \qquad E = kCRT^2 \, ln \frac{d}{D}.$$

The value of the product 10^4Ck is given in Table XI, but we can draw no conclusion of interest from the result. Equation 7, as has been shown in the papers cited, is not exactly true at very low vapor pressures for the liquid, but the error is probably not so great as one calorie for any of the non-associated substances over the entire range of temperature covered by the present investigation. The errors introduced by equation 7 are therefore far less than the errors of equation 2 with which it was combined.

Equation 13 is similar to equation 9 in its suggestion of a division of the total surface energy into two parts, one due to the liquid and the other due to the vapor. The resulting equations can be written,

$$14. \qquad E_L = K''RT^2 \, ln \, d,$$

$$15. \qquad E_V = K''RT^2 \, ln \, D,$$

$$16. \qquad E_L - E_V = E = K''RT^2 \, ln \frac{d}{D},$$

where $K'' = Ck$. These relations will also be further studied.

In conclusion, we differ from the arguments and conclusions advanced in the papers by Kleeman already cited at many points, but we would call particular attention to but two things: *First.*—In the investigation of the *inverse fifth power* law of the molecular attraction[1] he uses data from the papers already cited on molecular attraction by Mills. He ignores the fact that in those papers it has been shown that the assumption of the *inverse square* law of the distance gives a consistent agreement with the data over the entire range of temperature, not only for the substances that he investigates but for numerous others. Also when the results within 20° of the critical temperature are left out of consideration Kleeman obtains a consistent decrease of about 25 per cent. in his results at different temperatures. If the attractive force did not vary with the temperature, the greatest allowable variation from the mean to be attributed to the usual errors in the data should be 2 per cent., and we have shown that the *inverse square law* gives results within this limit—and usually far within this limit—for eight substances investigated gave no divergence from the mean greater than 1 per cent.

Second.—To explain the variation he obtains, Kleeman thinks that the force of attraction may diminish with rise of temperature. The papers by Mills as cited find that as regards the molecular attraction all of the evidence disproves this position, and as regards the chemical attraction,

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[1] *Phil. Mag.*, **19**, 795 (1910)

the possibility of a change of attraction with temperature was further especially considered in a paper on chemical energy,[1] and no evidence whatever for such a belief was found in the case investigated.

Summary.

1. The relation proposed by Whittaker that "The surface energy of a liquid in contact with its own vapor at any temperature is proportional to the product of the internal latent heat and the (absolute) temperature" has been investigated and the conclusion drawn that the relation is only approximately true.

2. The relation is shown to suggest a division of the so-called surface energy of a liquid into two parts, one part due to the liquid surface and the other to the surface of the vapor over the liquid. Further investigation of this suggestion is promised.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE ADIABATIC DETERMINATION OF HEATS OF SOLUTION OF METALS IN ACIDS.

PART II. THE HEAT OF DILUTION OF THE ACID SOLUTIONS.

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Introduction.

An account of a new series of determinations of the heat of solution of five metals in fairly concentrated acids was published in a recent number of THIS JOURNAL.[2] There it was shown that the heats of dilution, both of the acids and of the residual solutions after the reactions had been completed, affect the result much more than has usually been supposed. It was made clear that the actual results of the heats of solution of the metals in fairly concentrated acids must receive large corrections in order that they may all be reduced to the common standard of the heat of solution of the metal in the theoretical amount of acid of the standard dilution $HCl.200H_2O$. The actual attainment in a single experiment of this theoretical result is not possible because the completion of the reaction of the theoretical quantities would require an exceedingly long time, and therefore could not be measured with precision in the calorimeter.

As an example of the correction of the results, the case of zinc may be cited. In a single experiment 7.496 grams of pure zinc were dissolved in 941.4 grams of acid of the concentration $HCl.20H_2O$, and in the process 3461.0 calories of heat were evolved. This amount of zinc is 0.11467 gram atom, and the solution actually in the calorimeter contained 2.372

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[1] *Trans. Am. Electrochem. Soc.*, 14, 35 (1908).

[2] Richards and Burgess, THIS JOURNAL, 32, 431 (1910).